

# PATENT SPECIFICATION

779,972



Date of Application and filing Complete Specification Sept. 2, 1955.

No. 25264/55.

Application made in United States of America on Sept. 29, 1954.

Complete Specification Published July 24, 1957.

Index at acceptance:—Classes 7(6), B2Q(3C: 13); and 82(2), E3, F1(G1: L), F(2A: 3C: 3D: 4E: 4F: 4K), M.

International Classification:—C23c, g. F02f.

## COMPLETE SPECIFICATION

### Improvements relating to the Coating of Metal Articles with Aluminium

We, GENERAL MOTORS CORPORATION, a Company incorporated under the laws of the State of Delaware in the United States of America, of Grand Boulevard in the City of Detroit, State of Michigan, in the United States of America (Assignees of DEAN KNEALE HANINK, ROBERT FRANCIS THOMSON and ALBERT ACKERMAN SHOUDY, Jr.), do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods of coating metal articles with aluminium or aluminium alloy to form on them a layer which is actually alloyed to the underlying metal.

The word "aluminium" is hereinafter used to connote both commercially pure aluminium and alloys of aluminium. Primarily such alloys are those which contain at least 80% of commercially pure aluminium.

The methods according to the invention involve no dipping of the article into molten aluminium. They have been evolved for the purpose of coating the heads of poppet valves for internal combustion engines, especially the seating surface of the head; and such surface may be the only part coated. Not only valves of ferrous metal may be treated by the invention, but also those of other metals; such as titanium or titanium base alloys, nickel-base alloys, and molybdenum or alloys of it, so long as the valve metal does not have a very high solubility in aluminium.

Articles other than poppet valves may be treated if they are of convenient shapes and sizes. Examples are nuts and bolts, tubing, wire, woven metal fencing.

The scope of the invention is defined by the appended claims; how the invention may be carried out is particularly described with reference to the accompanying drawing and in terms of the treatment of poppet valves.

In the drawing:—

Fig. 1 is a vertical elevational view of a

poppet valve to be coated by one method;

Fig. 2 is a photomicrograph of a section through the valve seating face of a coated valve.

In each instance the surfaces of the valve to be coated are preferably cleaned prior to the aluminium coating and alloying operation. One satisfactory method is to clean them in a molten electrolytic caustic salt (for example a commercially available product called Kolene) at a temperature of approximately 900° F. The valves then may be washed in water and thereafter preferably further cleaned by acid pickling. An example of a suitable acid pickling bath is an aqueous solution containing about 2% hydrofluoric acid, 7% sulphuric acid and 10% nitric acid. In some instances the valves may require only a simple degreasing treatment in a chlorinated solvent. Mechanical cleaning methods, such as grit blasting, sand blasting etc., may be employed in some cases to supplement chemical treatment.

After the valves have been cleaned, any portions thereof which will be contacted by aluminium but which are not to be coated thereby may be treated with an appropriate stop-off coating to prevent any aluminium from bonding to or alloying with the base metal at such surfaces. A suitable stop-off material for this purpose is a sodium silicate solution, such as an aqueous solution containing approximately 20% to 50% sodium silicate. This step is not essential however, and merely omitting to degrease or pickle selected areas of the valves will frequently prevent the aluminium from adhering to these areas.

The aluminium with which the valve head is to be coated is then applied to the valve, as aluminium powder applied as a paste or paint, or as a molten metal spray. The latter is commonly referred to as metallized coating. An example of the aluminium paste or paint which may be used in accordance with the invention is a mixture of aluminium powder with suitable amounts of a vehicle, such as low ash-content lacquer or resin solution liquid lucite or

[Price 3s. 6d.]

a water solution of salt flux. If a salt flux is mixed with the aluminium powder to constitute the paste, it is advantageous to employ a salt flux which is capable of fluxing or cleaning the steel. Hence an aqueous solution of the same salt which is used as the fluxing or heating bath hereinafter described may be advantageously employed as a vehicle for the aluminium powder. Thus the surface may be fluxed by the paste applications alone; and in that case immersion in molten flux may be omitted, and the aluminium melted by some other method of heating.

For the paste, or paint, good results are obtained when approximately 30% to 50% by volume of aluminium powder, preferably between 200 and 400 mesh, is mixed with 10% to 20% by volume of binder solution and about 30% to 50% by volume of an appropriate thinner or solvent. Acetone or other commercial thinners may be employed. The above ranges of the constituents in the paste composition are not critical and a very wide variation in the composition may be used to obtain satisfactory results.

In accordance with one possible procedure, an aluminium paste or paint is applied to the surfaces of the valve which it is desired to coat. A heating operation is thereafter employed to uniformly distribute the aluminium over the surfaces to be coated and to securely bond the coating to these surfaces. After the paste has been applied to the valve by painting or spraying, the valve is immersed in a molten salt flux to a depth sufficient to cover the paste and the portions of the valve to be coated. The paste should be allowed to dry before immersing the valve in the salt so as to avoid introducing volatile matter into the hot salt.

Referring to the drawing, the poppet valve 10 shown in Fig. 1 is preferably immersed to the approximate depth indicated by the broken line a—a. In this position, the head 12 and neck 14 of the valve, as well as the paste 16, are completely below the surface of the molten salt. The valve is retained in the salt bath for a period of time sufficient to permit the hot salt to melt the aluminium paste and cause the molten aluminium to be distributed in a thin layer over the surfaces of the valve to be coated. Satisfactory results are normally obtained if this immersion period is of sufficient duration so that the immersed article is at a temperature of at least 1275° F. for a few seconds, say up to approximately 90 seconds. Preferably however the valve is retained in the salt for at least 15 seconds after it has reached this temperature. A heating and fluxing period in the salt of about 45 seconds to 90 seconds is typical.

It is preferred to use a fused salt bath consisting, by weight, of 37% to 57% KCl, 25% to 45% NaCl, 8% to 20%  $\text{Na}_3\text{AlF}_6$ , and 0.5% to 12%  $\text{AlF}_3$ . Such a salt flux should be maintained at a temperature of 1275° F. to 1400° F., a bath temperature between 1325°

F. and 1375° F. being the most desirable.

After the aluminium on the valve has been melted by immersion in the salt bath, the valve should be rapidly moved, e.g. rotated or vibrated, to properly distribute the aluminium over all the valve surfaces which it is desired to coat. Rotation or reciprocation, particularly rapid vertical oscillation, of the valve is effective in breaking the surface tension effect of the aluminium and causing of spreading the aluminium over the valve surfaces. For example, rotation of a poppet valve at a rate of 150 rpm has proved to be successful. However, rapid rotation may distort the valve head, and most satisfactory results are produced if the fluxed valve having the coating of molten aluminium thereon is rapidly reciprocated in a direction longitudinally of the axis of valve stem 18. Reciprocating motion having an amplitude of approximately  $\frac{1}{2}$  inch at a frequency of about 60 cycles per minute is satisfactory. Amplitudes less than 0.005 inches with a 60 cycle per second frequency may also be used, however, and produce excellent results. The agitation period need only be very short, from a few seconds to about 90 seconds. Depending upon the size and complexity of the article being coated with aluminium, an agitation period between 5 seconds and 60 seconds is preferred.

Although some distribution of the coating metal is possible if this agitation occurs immediately after withdrawal from the salt bath, it is best to agitate the valve while still immersed in the fused salt. Vibration in air results in a somewhat more irregular coating because of rapid cooling of the aluminium coating and is therefore not recommended for applications which require a very precise fit between the coated areas and mating parts.

If the aluminium coating is sufficiently uniform after agitation in the salt bath, the valve may be air cooled directly after removal from the salt flux. It is preferable in most instances to air cool the valve below 800° F. followed by a water quench. If maximum smoothness of the aluminium coating is not of prime importance, the coated article may be quenched in water before the aluminium has solidified. In any event the valve should be washed in water to remove adhering salt.

It should be noted the salt has a fluxing action even though the areas of the valve to be coated are covered with aluminium paste when the valve is dipped into the salt flux. This occurs because the paste comprises a multiplicity of small globules which permit the salt to contact the base metal to a sufficient extent to provide proper fluxing.

Alternatively, rather than applying a thick paste by means of a brush, the paste may be applied in the form of a thinner "paint" by spraying. As a further alternative, the aluminium also may be applied as a metal spray in which fine globules of hot, molten aluminium



are sprayed against the valve. If molten metal spraying is employed, it is normally desirable that the base material have a relatively rough surface in order that the aluminium will properly adhere to it.

In Fig. 1 the aluminium paste 16 is shown applied as an annular layer which overlaps both the seating face 20 of the valve and a portion of its neck 14.

- 10 The length of time the valve is permitted to remain in the salt bath for the purpose of melting and distributing the aluminium is dependent upon the size and shape of the valve. In the case of typical poppet valves for internal  
15 combustion engines, a heating period of approximately one minute in the salt bath followed by a vibration period of one minute in the bath has proved to be highly satisfactory. On the other hand, if the article to be coated  
20 is first heated in a furnace or by other suitable means before applying the aluminium, the dipping time in the salt can be appreciably reduced. For example, such preheating of a poppet valve to a temperature of 1000° F. or  
25 1100° F. permits the use of a salt dip of only a few seconds duration. Hence, the dipping period may be defined as that time required to raise the article to be coated to a temperature between 1275° F. and 1400° F.

- 30 The amounts and composition of the aluminium paste or the thickness of the aluminium applied to the valve governs the thickness of the aluminium coating. Since the valve seating face normally is the only portion  
35 of the valve in which the aluminium coating layer thickness is critical, it is this area which determines whether excess aluminium has been deposited.

- In some instances, however, it may be better  
40 to apply aluminium in an amount exceeding the quantity actually required as a coating layer because of difficulty in distributing the metal over all of the surfaces during the coating or alloying step. The excess coating metal may  
45 be removed by mechanical or pneumatic methods.

- In the photomicrograph shown in Fig. 2 the base metal of the valve is indicated at 24, while  
50 26 indicates the alloy of aluminium with the base metal and 28 the outer layer of aluminium. If the valve is made of ferrous metal, the layer 26 is a complex iron-aluminium alloy.

- The aluminium-base metal alloy layer 26 produced normally ranges from about 0.0005  
55 inch to 0.0015 inch in thickness, while the aluminium overlay 28 does not exceed approximately 0.004 inch. In the case of automobile poppet valves, it is preferred to have the outer aluminium layer between 0.0005 inch and  
60 0.0015 inch thick, resulting in a combined thickness of the iron-aluminium alloy layer and the aluminium overlay of approximately 0.001 inch to 0.0025 inch. A coating layer of this thickness has demonstrated superior yielding  
65 characteristics when the valve seating face is

"pounded in" during service. Small depressions in the seating face of the valve caused by engine deposits which become lodged between the valve seating face and valve seat during operation remain protected by the surface alloy layer.

When the flux is incorporated in an aluminium paste applied to the article, the aluminium may be melted by heating the article or a portion thereof in a furnace, or by  
75 flame heating or induction heating. In order to obtain a proper bond between the aluminium and base metal to be coated, a reducing or inert atmosphere is required.

When the article is heated outside a salt  
80 flux bath in the foregoing manner, the aluminium should still reach a temperature between 1275° F. and 1400° F. in order to effectively coat the article.

What we claim is:—

1. The method of forming on a metal article  
85 an aluminium coating alloyed to the surface thereof, which method comprises painting or spraying on to the article a coating of aluminium-containing material, and then heating  
90 the article while the coating is in contact with a salt flux containing potassium chloride, sodium chloride, cryolite, and aluminium fluoride, so that the aluminium is caused to alloy with the surface.

2. The method of forming on a metal article  
95 an aluminium coating alloyed to the surface thereof, which method comprises painting or spraying on to the article a mixture of aluminium-containing material and a salt flux  
100 containing potassium chloride, sodium chloride, cryolite, and aluminium fluoride, and heating the article so that the aluminium is caused to alloy with the surface.

3. The method of forming on a metal article  
105 an aluminium coating alloyed to the surface thereof, which method comprises painting or spraying on to the article a coating of aluminium-containing material, and then  
110 immersing the article in a molten salt flux containing potassium chloride, sodium chloride, cryolite, and aluminium fluoride, thereby heating the article so that the aluminium is caused to alloy with the surface.

4. The method according to Claim 1, 2 or 3,  
115 wherein the salt flux consists of:—

37 to 57% KCl  
25 to 45% NaCl  
8 to 20%  $\text{Na}_3\text{AlF}_6$   
0.5 to 12%  $\text{AlF}_3$   
120

5. The method according to Claim 3, or Claim 4 is so far as appendant to Claim 3,  
125 wherein the article is rapidly moved, as by vibration or rotation, while immersed in the flux.

6. The method according to Claim 4, wherein the temperature of the molten flux is between 1275° F. and 1400° F.

7. The method of forming on a poppet valve  
130 an aluminium coating alloyed to the surface

thereof, which method comprises painting or spraying on to the article a coating of aluminium-containing material, and then heating the valve while the coating is in contact  
5 with a salt flux comprising:—

37 to 57% KCl  
25 to 45% Na Cl  
8 to 20%  $\text{Na}_3\text{AlF}_6$   
0.5 to 12%  $\text{AlF}_3$

whereby the aluminium is caused to alloy with 10 the surface.

8. The method of forming an alloyed aluminium coating on a poppet valve substantially as hereinbefore particularly described with reference to the accompanying drawing. 15

E. WILLIAMSON,  
Chartered Patent Agent.

Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which  
Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press,—1957.  
copies may be obtained.

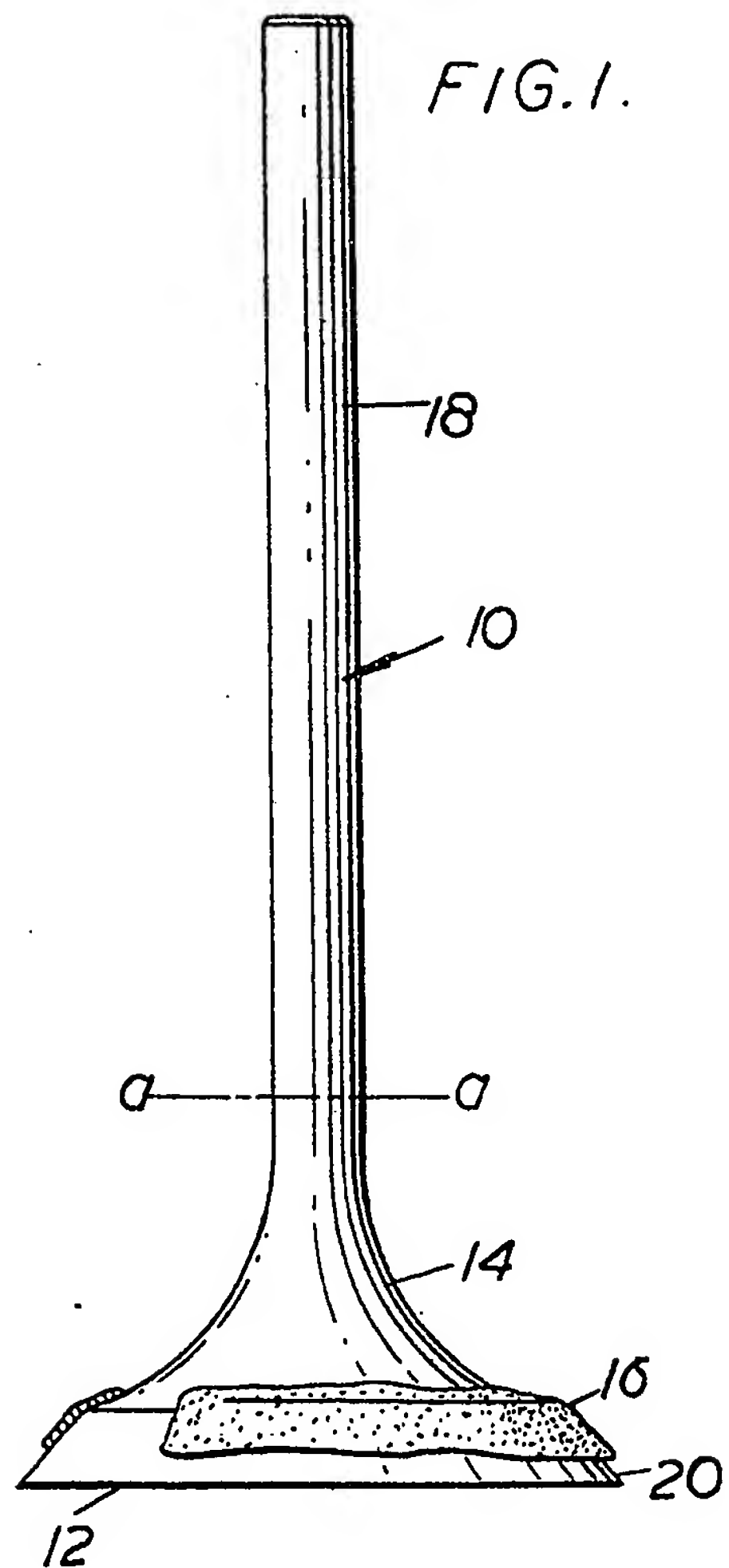


FIG. 2.

